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DOI:

[10.1016/j.chemosphere.2017.11.068](https://doi.org/10.1016/j.chemosphere.2017.11.068)

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Document Version

Peer reviewed version

Citation for published version (Harvard):

Stubbings, WA & Harrad, S 2018, 'Leaching of TCIPP from furniture foam is rapid and substantial', *Chemosphere*, vol. 193, pp. 720-725. <https://doi.org/10.1016/j.chemosphere.2017.11.068>

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Accepted Manuscript

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PII: S0045-6535(17)31845-3

DOI: [10.1016/j.chemosphere.2017.11.068](https://doi.org/10.1016/j.chemosphere.2017.11.068)

Reference: CHEM 20265

To appear in: *ECSN*

Received Date: 17 September 2017

Revised Date: 10 November 2017

Accepted Date: 14 November 2017

Please cite this article as: Stubbings, W.A., Harrad, S., Leaching of TCIPP from furniture foam is rapid and substantial, *Chemosphere* (2017), doi: 10.1016/j.chemosphere.2017.11.068.

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1 **LEACHING OF TCIPP FROM FURNITURE FOAM IS RAPID AND**
2 **SUBSTANTIAL**

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19 Abstract

20 A series of laboratory experiments were conducted, in which waste furniture polyurethane
21 foam samples containing tris (1-chloro-2-propyl) phosphate (TCIPP) were contacted with a
22 range of leaching fluids, formulated to simulate the composition of landfill leachate.
23 Leaching was examined under a number of different scenarios, such as: dissolved humic
24 matter concentration, pH, and temperature, as well as the effect of agitation, and
25 waste:leaching fluid contact duration. In addition to single batch (no replenishment of
26 leaching fluid), serial batch (draining of leachate and replenishment with fresh leaching fluid
27 at various time intervals) experiments were conducted. Leaching of TCIPP from PUF appears
28 to be a first order process. Concentrations of TCIPP in leachate generated by the
29 experiments in this study ranged from 13 mg L^{-1} – 130 mg L^{-1} . In serial batch leaching
30 experiments, >95% of TCIPP was depleted from PUF after 168 h total contact with leaching
31 fluid. Our experiments indicate leaching is potentially a very significant pathway of TCIPP
32 emissions to the environment.

33

34 Keywords

35 Tris (1-chloro-2-propyl) phosphate;

36 Polyurethane foam;

37 Landfill;

38 Chlorinated phosphate flame retardants;

39 Leaching

40

41 1. Introduction

42 A widely used group of flame retardants are the chlorinated phosphorous flame retardants
43 (PFRs) also known as phosphinates, such as tris(1-chloro-2-propyl)phosphate (TCIPP), tris(2-
44 chloroethyl)phosphate (TCEP) and tris(1,3-dichloroisopropyl)phosphate (TDCIPP). These and
45 other PFRs have been applied to a wide range of commercial products such as: textiles,
46 rubber, polyurethane foam (PUF), cellulose, cotton, electronic equipment cables, casting
47 resins, glues, engineering thermoplastics, epoxy resins, and phenolic resins to meet and
48 comply with fire safety codes, standards and regulations (van der Veen and de Boer, 2012).
49 TCIPP has been found to be resistant to degradation (Leisewitz et al., 2000; Kawagoshi et al.,
50 2002). PFR contamination of indoor air and dust, lakes, river sediment and marine biota
51 across Europe, USA and Japan is well documented (Carlsson et al., 1997; Marklund et al.,
52 2003; Andresen et al., 2004; Björklund et al., 2004; Stapleton et al., 2009; Leonards et al.,
53 2011). Moreover, detection of TCIPP and TCEP in groundwater older than 20 years indicates
54 considerable persistence in aquifers (Regnery et al., 2011). In laboratory experiments,
55 Regnery and Püttmann (2010) demonstrated that TCEP and TCIPP appeared resistant to
56 photodegradation by sunlight. Furthermore, particulate-bound TDCIPP has been shown
57 capable of mid to long-range transport due to its highly persistent nature in the atmosphere
58 with regard to OH radical oxidation (Liu et al., 2014). TCIPP accumulates in the liver and
59 kidneys (Leisewitz et al., 2000), with work by Dishaw et al., (2011) showing it decreases cell
60 number and alters neurodifferentiation. "Skin and eye irritations in animals are
61 unquestioned " (Leisewitz et al., 2000) and is considered potentially carcinogenic (Ni et al.,
62 2007). Concerns over such health impacts are exacerbated by the detection of a metabolite
63 of TCIPP, bis(1-chloro-2-propyl)phosphate (BCIPP) in human urine (Dodson et al. 2014).

64 Notwithstanding this combination of suspected health effects and demonstrable human
65 exposure, in 2000 the total TCIPP production in Europe was 36,000 tonnes. It is used in
66 applications such as rigid foams in the production of construction blocks and panels used for
67 insulation purposes, and in flexible PUF for soft furnishings and mattresses (EU RAR, 2008).
68 Currently, used furniture polyurethane foams treated with TCIPP are treated as municipal
69 rather than hazardous waste, and are thus landfilled or incinerated. In the UK alone, it is
70 estimated that around 670,000 tonnes of furniture of which a proportion will be PUF was
71 disposed of by householders annually (WRAP, 2012). This reservoir of TCIPP within furniture
72 polyurethane foams has and will continue to gradually enter the waste stream. An EU risk
73 assessment report (EU RAR, 2008) predicts that a typical UK landfill with a leachate flow of
74 $100 \text{ m}^3 \text{ day}^{-1}$ would emit a maximum TCIPP mass via leachate of 6.7 g day^{-1} . There is hence a
75 pressing need to understand the fate of chemicals like TCIPP associated with furniture PUF
76 following disposal. Potential emission pathways for chemicals associated with landfill
77 include contamination of leachate and volatilisation (Stubbings and Harrad, 2014). The
78 physicochemical properties of TCIPP (water solubility = $1,600 \text{ mg L}^{-1}$ at $20 \text{ }^\circ\text{C}$, vapour
79 pressure = $1.4 \times 10^{-8} \text{ Pa}$ at 21°C and $\text{Log } K_{\text{ow}} = 2.59$ (van der Veen and de Boer, 2012;
80 Tremain, 2002)), suggest that following disposal to landfill such leaching and volatilisation of
81 TCIPP associated with treated PUF may be extensive. TCIPP is an additive chemical not
82 covalently bound to the PUF material and therefore TCIPP escape is relatively facile. Considering
83 that these products are often treated with TCIPP at percent levels by weight (EU RAR, 2008),
84 it is apparent that furniture PUF constitutes a significant potential source of TCIPP to the
85 environment. Despite this, very little research has been undertaken that examines end-of-
86 life management of TCIPP associated with waste soft furnishings (items made of cloth, such

87 as curtains, chair coverings, etc., used to decorate a room) and furniture. In the absence to
88 our knowledge of empirical data related to the fate of TCIPP treated furniture foam in
89 landfill, this study conducts a series of controlled laboratory experiments to test the
90 hypothesis that TCIPP is capable of leaching from waste furniture PUF.

91

92 **2. Materials and methods**

93 **2.1. Samples**

94 We investigated a flame retardant-treated polyurethane foam sample taken from a sofa
95 cushion. The sample was collected from a sofa prior to entry into the UK waste stream in
96 Birmingham, UK, 2012. As the presence of flame retardants present in the foam was
97 unknown, its chemical content was determined prior to deployment in our leaching
98 experiments. To do so, small pieces of foam (approx. 5 mm × 5 mm × 5 mm) were taken
99 from random points from the sample totalling approximately 50 mg. An accurately weighed
100 aliquot of foam (50 mg) and 5 mL of ethyl acetate were added to a pre-washed test tube,
101 vortexed for 1 min and sonicated for 5 mins before being centrifuged for 2 mins at 2000
102 rpm. The supernatant was transferred to a clean tube, the extraction was repeated and both
103 supernatants were combined (10 mL total) and vortexed for 1 min. 1 mL of sample was then
104 transferred to a clean tube and diluted using 9 mL ethyl-acetate. Finally 10 μ L of the first
105 dilution was transferred to and diluted further using 90 μ L methanol containing 90 ng d_{15} -
106 labelled TPhP as internal standard (x10,000 dilution in total). The test PUF was analysed via
107 LC-MS/MS (see section 2.4) in quintuplicate.

108

109 2.2. Leaching test methods

110 Four distinct experimental scenarios were undertaken to examine the effects of: (a) contact
111 time (single batch experiments); (b) duration of serial or periodic wetting and draining of
112 waste (serial batch experiments); (c) temperature (20, 50, and 80 °C); and (d) pH level (acidic
113 5.8, slightly acidic 6.5, and alkaline 8.5) of the leaching fluid on the leachability of the target
114 analyte from the sample material (SI; Table S1). In scenario (a) contact time, the treated
115 sample is contacted once with the leaching fluid for a set predetermined time of either, 6 h,
116 24 h or 48 h. In scenario (b) serial batch, the sample is contacted with the leaching fluid for
117 168 h in total, with the resulting leachate being removed from the contact vessel and
118 replenished with fresh leaching fluid 6 times, at intervals of 6 h (batch 1), 24 h (batch 2), 48
119 h (batch 3), 72 h (batch 4), 96 h (batch 5) and 168 h (batch 6). The leachate was extracted
120 from the contact vessel via pouring or draining through a 0.45 μm pore size glass fibre filter
121 (Advantec, Japan), in which the contact vessel was inverted for approximately 5 mins to
122 ensure as much leachate was removed as possible. Each batch of leachate were analysed for
123 analyte concentrations at the given intervals. Leaching fluids were prepared as previously
124 described in Stubbings and Harrad, 2016. PTFE bottles (500 mL) were used as contact
125 vessels during controlled leaching experiments. The contact vessel was not completely filled
126 with leaching fluid and as a result headspace was present inside the contact vessel. In all
127 experiments, 1 g of PUF sample was contacted with 100 mL of Milli-Q water giving a liquid-
128 solid ratio of 100:1 (v/w). Following addition of the sample and leaching fluid, contact
129 vessels were horizontally agitated on a mechanical shaker at 200 rpm for the desired
130 contact time. In scenario (c) samples examining the influence of temperature, the contact
131 vessels were not agitated and instead were submerged in a water bath for 24 h at the

132 desired temperature. In scenario (d) experiments were agitated at 200 rpm for 6 h and the
133 initial pH of the leaching fluid before contact with flame retarded PUF samples was
134 recorded. Each of the above leaching experiments were conducted in duplicate.

135

136 **2.3. Sample preparation and chemical analysis**

137 Each leachate sample was filtered through a 0.50 μm size particle retention glass fibre filter
138 (Advantec, Japan) to remove any textile fibres from the leachate and then spiked with 10 μg
139 of d_{15} -labelled Tri-phenyl-phosphate (TPhP) as internal (or surrogate) standard. The filtrate
140 was then extracted in series using 2 x 50 mL dichloromethane (DCM) by liquid-liquid
141 extraction with mechanical shaking for 30 mins each time. Approximately 5-10 mL 2% NaCl
142 solution was used to enhance separation after extraction. The combined DCM extracts were
143 dried via filtration through Na_2SO_4 . The dried extract was concentrated to 0.5 mL using a
144 Zymark Turbovap II with solvent exchange to *n*-hexane before being loaded on to a 2 g pre-
145 cleaned, activated florisil column and washed with 20 mL *n*-hexane. The TCIPP was then
146 eluted using 20 mL ethyl acetate. The eluate was evaporated to incipient dryness and then
147 reconstituted to 100 μL with addition of 25 ng d_{27} -labelled TnBP as a recovery standard in
148 methanol. Prior to analysis via LC-ESI-MS/MS the samples underwent further dilution in
149 which a 10 μL aliquot was taken and diluted with 990 μL of methanol, and then an
150 additional 10 μL aliquot of that first 1 mL dilution was taken and diluted with 990 μL of
151 methanol to yield a 10,000 times dilution. This was necessary due to the very high
152 concentrations of TCIPP in samples.

153

154 2.4 Determination of concentrations of TCIPP

155 Concentrations of TCIPP in all samples generated in experiments were using a dual pump
156 Shimadzu LC-20AB Prominence high pressure liquid chromatograph (Shimadzu, Kyoto,
157 Japan) equipped with a Sciex API 2000 triple quadrupole mass spectrometer (Applied
158 Biosystems, Foster City, CA, USA) (see SI for additional details).

159

160 2.5. Calculation of TCIPP leaching

161 The percentage of TCIPP present in PUF that was leached into each leachate sample (PL)
162 was calculated as previously defined by Stubbings and Harrad, (2016) (equation 1):

163 Equation 1: $PL = \left[\frac{C_{leachate} \times V}{C_{waste} \times W} \right] \times 100\%$

164

165 PL = percentage leached (%)

166 $C_{leachate}$ = Concentration of TCIPP in leachate (mg/L)

167 V = volume of leachate (L)

168 C_{waste} = Concentration of TCIPP in PUF (mg/kg)

169 W = weight of PUF sample subjected to leaching (kg)

170 The percentage of TCIPP leached normalised to contact time (PLT , % h^{-1}) is calculated
171 according to equation 2.

172 Equation 2: $PLT = \frac{PL}{t}$

173 PL = percentage leached (%)

174 t = contact time (h)

175

176 **2.3. Data analysis**

177 Basic and descriptive statistics were calculated using IBM SPSS Statistics 24, and Microsoft

178 Excel 2013 software. Plots were generated by Microsoft Excel 2013.

179

180 **3. Results and discussion**

181 **3.1. Initial TCIPP concentrations in the furniture PUF samples**

182 The average \pm standard deviation concentration of TCIPP determined in five 50 mg sub-
183 samples of the PUF sample used in this study was $17,000 \pm 13 \text{ mg kg}^{-1}$ or 1.7% by weight.

184 This is consistent with information provided to the authors that TCIPP is typically added to
185 flexible PUF at 1-4% by weight (pers. comm. Flexible Foam Research Ltd, 2014).

186

187 **3.2. Effects of contact time on TCIPP leaching from single batch experiments.**

188 TCIPP concentrations in leachate (mg L^{-1}), as well as mean PL (%) and mean PLT values ($\% \text{ h}^{-1}$)

189 ¹) generated from the single batch experiments are provided in Table 1. There were no

190 significant ($p > 0.05$) differences in TCIPP concentrations in leachate generated via different

191 contact times. This suggests that contact time has comparatively little effect on TCIPP
192 leaching from furniture PUF, therefore leaching from the PUF material appears to occur in
193 the early stages of contact with the leaching fluid. The quantity of TCIPP being leached in
194 experiments exceeds substantially that observed for polybrominated diphenyl ethers
195 (PBDEs) from cathode ray tube (CRT) plastic housing (Stubbings and Harrad, 2016).

196

197 **3.3. Effect of cyclical wetting and draining on TCIPP leaching (serial batch experiments)**

198 Average concentrations of TCIPP (mg L^{-1}) detected in leachate and mean *PLT* values ($\% \text{ h}^{-1}$)
199 obtained from the serial batch experiments are presented in Figure 1, with TCIPP
200 concentrations, mean PL (%) and mean *PLT* values ($\% \text{ h}^{-1}$) for the same experiments
201 provided in SI (Table S6). After 6 h contact time, concentrations of TCIPP leached from
202 flexible PUF in these serial batch experiments diminish with increasing experimental
203 duration. However, the extent of TCIPP leaching from the material is substantial, and after a
204 cumulative 168 h of leaching, the cumulative total of TCIPP removed from the furniture
205 foam by the leaching fluids approaches 96% of the initial mass present in the PUF sample
206 (Figure 2). Overall – although longer term experiments are required to confirm this - this
207 serial batch experiment indicates that replenishment of leaching fluid as would be expected
208 in a landfill could result in the near-total removal of TCIPP from PUF via leaching over long
209 periods.

210

211 **3.4. Leaching kinetics**

212 Ho et al., (2005) expressed the leaching of water-soluble components from sapwood in
213 terms of the following second-order rate equation:

214 Equation 3:
$$\frac{Ct}{t} = k(Cs - Ct)^2,$$

215 where k is the second-order leaching rate constant ($L\ ng^{-1}\ min^{-1}$), C_s the leaching capacity,
216 which is the concentration of TCIPP at saturation ($ng\ L^{-1}$), and C_t is the concentration of
217 TCIPP ($mg\ L^{-1}$) in suspension at any given time, t (min). The leaching capacity, C_s , and the
218 second-order leaching rate constant, k , can be determined experimentally from the slope
219 and intercept by plotting t/C_t against t .

220 Plots were generated to evaluate whether TCIPP leaching from PUF could be explained using
221 second order leaching kinetics. In contrast to the analogous experiments with PBDEs
222 leaching from CRT plastic chips (Stubbings and Harrad, 2016) and hexabromocyclododecane
223 (HBCDDs) from textiles (Stubbings et al, 2016), the concentrations of TCIPP in leachates
224 from serial batch experiments were not included in generating these plots because the
225 greater removal of TCIPP from the foam resulted in significantly lower initial concentrations
226 in the PUF between batches. Therefore, only duplicate measured leachate concentrations in
227 single batch experiments conducted at 20 °C for each contact time (6 h, 24 h and 48 h) and
228 also for each DHM concentration were included in leaching kinetics calculations. Using the
229 equations described in Stubbings et al. (2016), t/C_t was plotted against t , where C_t is the
230 concentration of TCIPP ($mg\ L^{-1}$) in suspension at any given time and t (min). The resulting
231 plots are provided for DHM concentrations 0, 100 and 1,000 $mg\ kg^{-1}$ in the SI (Figure S2),
232 and show that the y-intercept and therefore k values are negative for each DHM

233 concentration. These data suggest that TCIPP leaching from PUF is not a second order
234 kinetic process.

235 To evaluate if the leaching of TCIPP from PUF is governed by first-order kinetics, we plotted
236 the natural logarithm of TCIPP concentration versus time (Figure 3). We generated such
237 plots for all single batch experiments conducted at 20 °C and for each DHM concentration.
238 The plots are linear with a negative slope in all instances; suggesting that leaching of TCIPP
239 from PUF may be a first-order process. A caveat is that these conclusions are based on only
240 6 data points per plot (duplicates at 3 contact times). Moreover, only the plot for the
241 experiments where the leaching fluid contained 100 mg L⁻¹ DHM was significantly linear ($p <$
242 0.05). However, the leaching fluid containing 0 mg L⁻¹ DHM was significant at a lower
243 confidence interval ($p < 0.10$). The slope, Y-intercept, the leaching rate constant, k (min⁻¹),
244 two-tailed p values, and Pearson's correlation coefficients, r , for these 1st order plots are
245 given in Table 2.

246 We offer here some possible explanations for why TCIPP does not fit with second order
247 kinetics as has been observed for HBCDD and PBDEs from fabrics and CRT plastic housing
248 chips (Stubbings et al. 2016; Stubbings and Harrad, 2016). Firstly, PUF is more porous,
249 permeable and has a larger surface area than other materials tested. This allows the
250 leaching fluid to access far greater surface area than in less porous materials. Secondly,
251 there are significant differences in the physicochemical properties between the chlorinated
252 phosphates and the brominated flame retardants, with TCIPP possessing an aqueous
253 solubility 20,000 – 800,000 times greater than PBDEs.

254

255 3.5. Effects of temperature on TCIPP leaching from furniture PUF samples.

256 Within a landfill, temperatures can sometimes reach as high as 80-90 °C due to heat
257 released during aerobic degradation (Kjeldsen et al., 2002). Therefore, the influence on *PLT*
258 of leachate temperatures of 20 °C, 50 °C and 80 °C were investigated. Leachate
259 concentrations for TCIPP from flexible PUF at different temperatures and DHM
260 concentrations are displayed in Figure 4. TCIPP concentrations, mean PL (%) and mean *PLT*
261 values (% h⁻¹) in these experiments (conducted in duplicate) are provided in SI (Table S7).
262 There are significant differences in TCIPP concentrations in the leachate between 50 °C and
263 80 °C for both DHM containing leaching fluids, while the differences between these
264 temperatures are significant at a lower confidence interval ($p = 0.059$) for deionised Milli-Q
265 leaching fluid. There is also a significant ($p = 0.057$) difference between TCIPP
266 concentrations in leachate generated at 20 °C and 50 °C when the leaching fluid was
267 deionised water. The lower TCIPP concentrations present in leachates at 80 °C relative to
268 those at 50 °C may be a result of enhanced TCIPP volatilisation at this higher temperature as
269 well as TCIPP potentially entering the headspace of the leaching vessel in the gas phase and
270 being lost when the vessel was subsequently opened.

271

272 3.6. Effects of pH on TCIPP leaching from furniture PUF.

273 The influence of leachate pH values of 5.8, 6.5 and 8.5, on TCIPP leaching behaviour was
274 investigated. Leachate concentrations values for TCIPP from flexible PUF at different pH
275 values and DHM concentrations are displayed in Figure 5. Duplicate TCIPP concentrations,

276 mean PL (%) and mean *PLT* values (% h⁻¹) for the same experiments are provided in the SI
277 (Table S8).

278 In leachates to which no DHM was added there were significant differences ($p < 0.05$) in
279 TCIPP concentrations between pH 5.8 and 8.5, and 6.5 and 8.5. In leachates in which 100 mg
280 L⁻¹ DHM was present, there were no significant differences in TCIPP concentrations between
281 the pH values studied. At 1,000 mg L⁻¹ there are significant differences between pH 5.8 and
282 8.5, and 6.5 and 8.5. The alkaline pH of 8.5 generated the highest concentrations of TCIPP in
283 the leachate for all three DHM concentrations explored. Generally, more alkaline leaching
284 fluids remove more TCIPP from the foam.

285

286 **3.7. Effects of agitation on TCIPP leaching from furniture PUF**

287 By comparing the results of experiments conducted at 20 °C using Milli-Q water with contact
288 times of 24 h with and without agitation, the effect of agitation on TCIPP leaching from the
289 PUF can be examined (SI; Figure S4). The results of a paired sample t-test are presented in SI
290 (Table S9) and indicate that there are significant differences ($p < 0.05$) in TCIPP
291 concentrations between agitated and non-agitated samples. The effect of agitation on
292 treated PUF is to enhance TCIPP leaching across all three DHM concentrations examined;
293 concentrations of TCIPP in agitated samples were on average 43% higher at 0 mg L⁻¹ DHM,
294 14% greater at 100 mg L⁻¹ DHM, and were elevated by 32% at 1,000 mg L⁻¹ DHM.

295

296 **3.8. Statistical analysis of the whole data set**

297 The results of multiple linear regression analysis (MLRA) for TCIPP treated flexible PUF are
298 provided in the SI (Table S10). The importance value ranks the effects of the independent
299 variables from greatest to smallest. Of the independent variables explored in these
300 experiments, the pH of the leaching fluid had the greatest effect on TCIPP concentrations.
301 The alkaline pH of 8.5 yielded the greatest TCIPP concentrations in leachate. The contact
302 time was significantly negatively correlated with TCIPP concentrations in leachate. This may
303 be due to greater degradation of TCIPP at longer contact times, but is more likely driven by
304 the inclusion of the serial batch experiments in the MLRA, in which concentrations of TCIPP
305 in the PUF were heavily depleted in subsequent batches, thereby yielding lower
306 concentrations at longer contact times. The DHM content of the leaching fluid was also
307 shown to exert a significant influence on TCIPP leaching from PUF, with higher DHM
308 concentrations leading to greater TCIPP concentrations in leachate. Finally, the effect of
309 leaching fluid temperature on TCIPP concentrations in leachate is not significant –
310 presumably the increased solubility of TCIPP at higher temperatures was offset by some
311 other factor, such as the aforementioned potential entry of TCIPP into the headspace of the
312 leaching vessel with subsequent loss on opening the vessel.

313

314 **4. Summary**

315 We present evidence that under laboratory conditions, leaching of TCIPP from furniture PUF
316 is extensive, occurs rapidly and appears to be a first order kinetic process. This suggests that
317 TCIPP in furniture foams disposed of at landfill is likely to readily leach into percolating
318 waters and that very substantial releases to leachate from such discarded foams are likely.

319 Given the widespread use of TCIPP in furniture foam, this study suggests that greater
320 knowledge of its presence and of other PFRs in landfill leachate is urgently required. More
321 research is required to ascertain how much TCIPP and other PFRs are removed at WWTPs
322 receiving landfill leachate in the UK by measuring effluent flows. It would also be of benefit
323 to measure the quantity of PFRs in influent flows, to calculate removal efficiencies.
324 Moreover, the potential for contamination of groundwater and drinking water with PFRs
325 should be explored.

326

327 **Acknowledgements**

328 The authors acknowledge gratefully the provision of an Open Competition CASE studentship
329 award to WAS by the UK Natural Environment Research Council (NERC ref NE/I018352/1).
330 Additional financial support to WAS from Ricardo-AEA is also acknowledged gratefully. The
331 research leading to these results has received funding from the European Union Seventh
332 Framework Programme (FP7/2007-2013) under grant agreement 295138 (INTERFLAME).

333

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412

413 **Table 1: Concentrations (mg L⁻¹) of TCIPP in leachate in duplicate experiments, together**
 414 **with mean PL (%) and mean PLT values (% h⁻¹) derived from contacting PUF with artificial**
 415 **leachate.**

DHM conc. (mg L ⁻¹)	Contact time (h)	TCIPP Conc. (mg L ⁻¹)	TCIPP Conc. (mg L ⁻¹)	PL (%)	PLT (% h ⁻¹)
0	6	59	67	36	6.0
0	24	29	22	15	0.61
0	48	16	36	15	0.31
100	6	60	67	36	6.0
100	24	61	68	37	1.6
100	48	49	47	28	0.58
1,000	6	70	69	40	6.7
1,000	24	89	63	44	1.8
1,000	48	45	68	33	0.68

DHM: dissolved humic matter; PL: percentage leached; PLT: percentage leached normalised to contact time.

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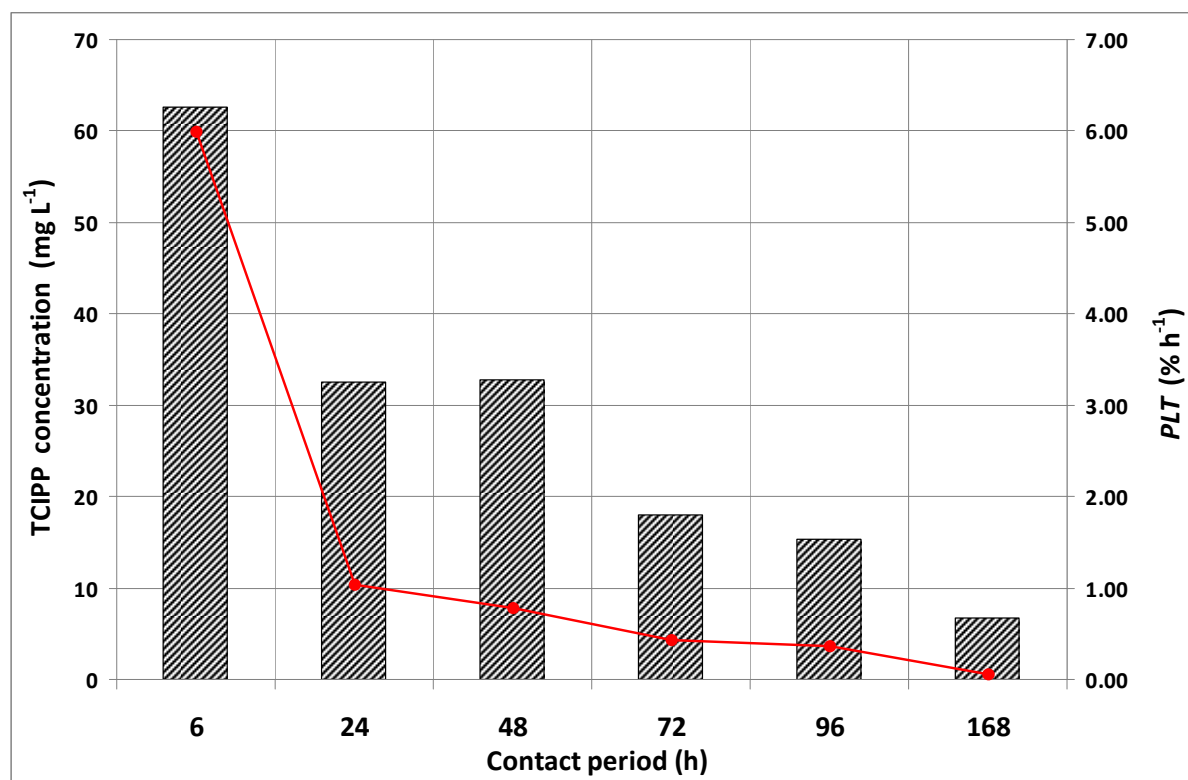
418 **Table 2: First order leaching rate slopes, y-intercepts, constants (k), and r values obtained**
 419 **from experiments examining the leaching of TCIPP from PUF.**

Constant / DHM Conc. (mg L ⁻¹)	Slope (log _e mg L ⁻¹ /min)	y-intercept (log _e mg L ⁻¹)	k (min ⁻¹)	Two-tailed p value	Correlation coefficient: r
0	-0.0004	4.1	0.000000031	.095	-0.737
100	-0.0001	4.2	0.000000030	.044	-0.824
1,000	-0.0001	4.3	0.000000022	.316	-0.497

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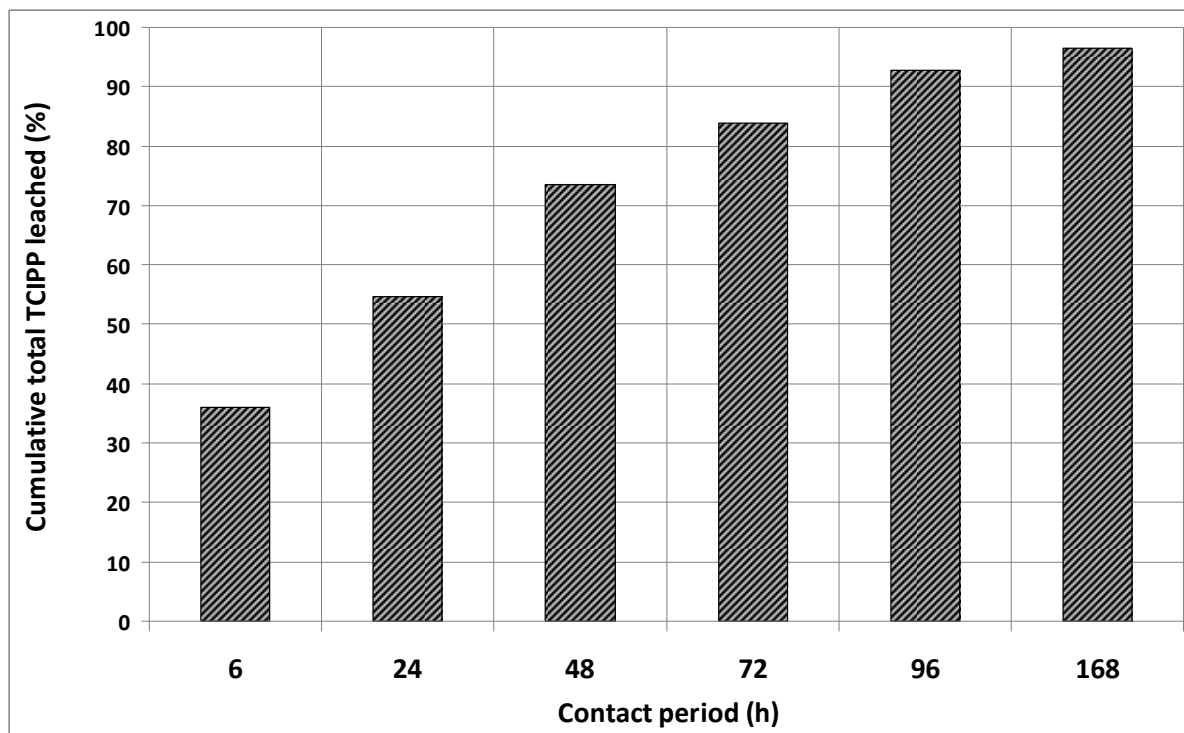


423

424 **Figure 1: Mean (n=2) TCIPP concentrations (mg L⁻¹; bars) and PLT (% h⁻¹) (red circles) in**
425 **leachate produced by experiments examining the effect of cyclical wetting and draining**
426 **(serial batch) on TCIPP leaching from PUF.**

427

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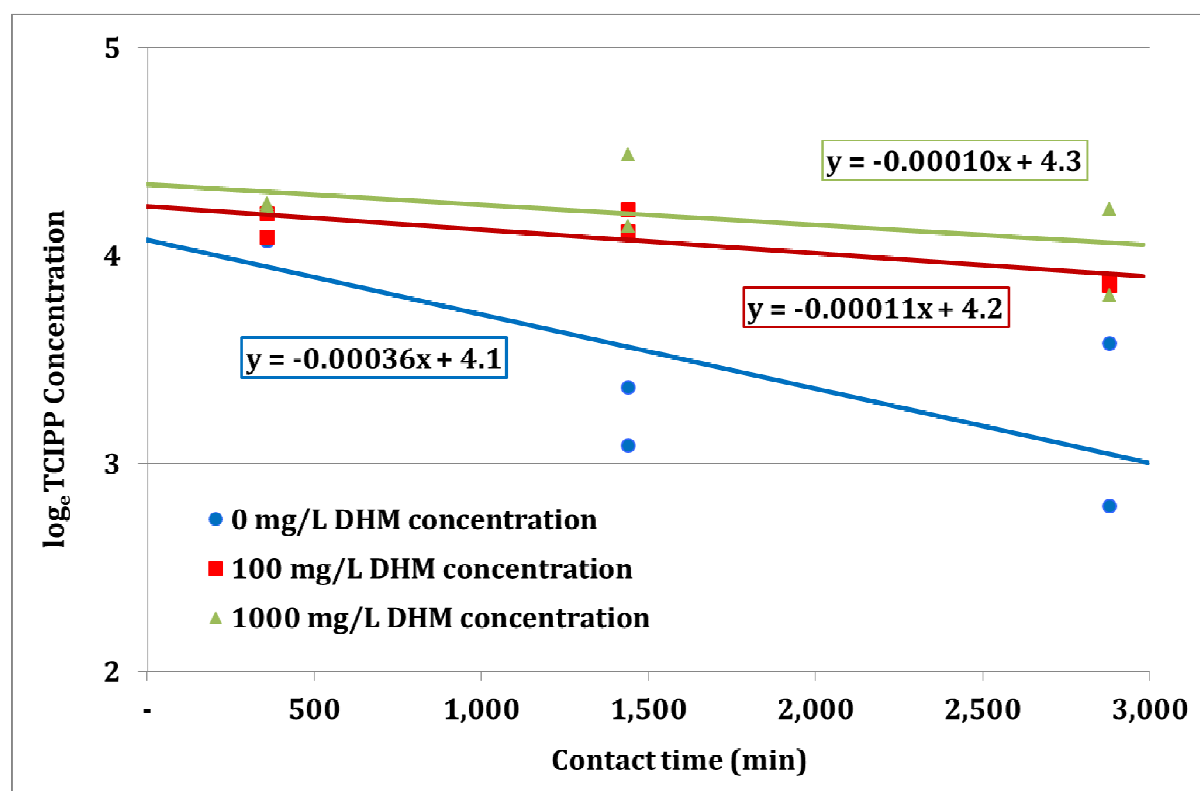


429

430 **Figure 2: Cumulative total TCIPP leached (% present in source PUF) during experiments**
431 **examining the effect of cyclical wetting and draining (serial batch) on TCIPP leaching from**
432 **PUF.**

433

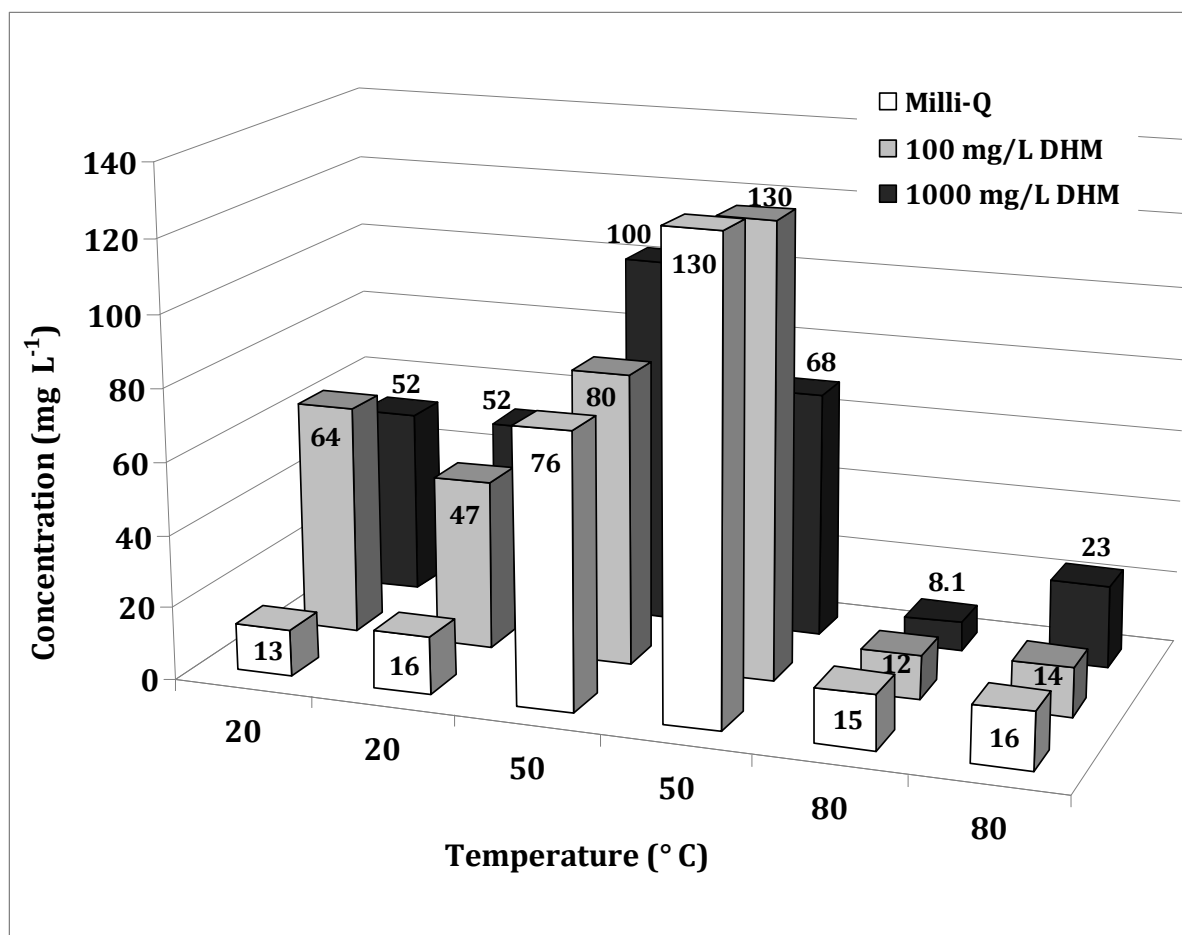
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436 Figure 3: Plot of natural logarithm of concentration of TCIPP in leachate versus time (t ,
437 min) in single batch experiments examining TCIPP leaching from PUF.

438

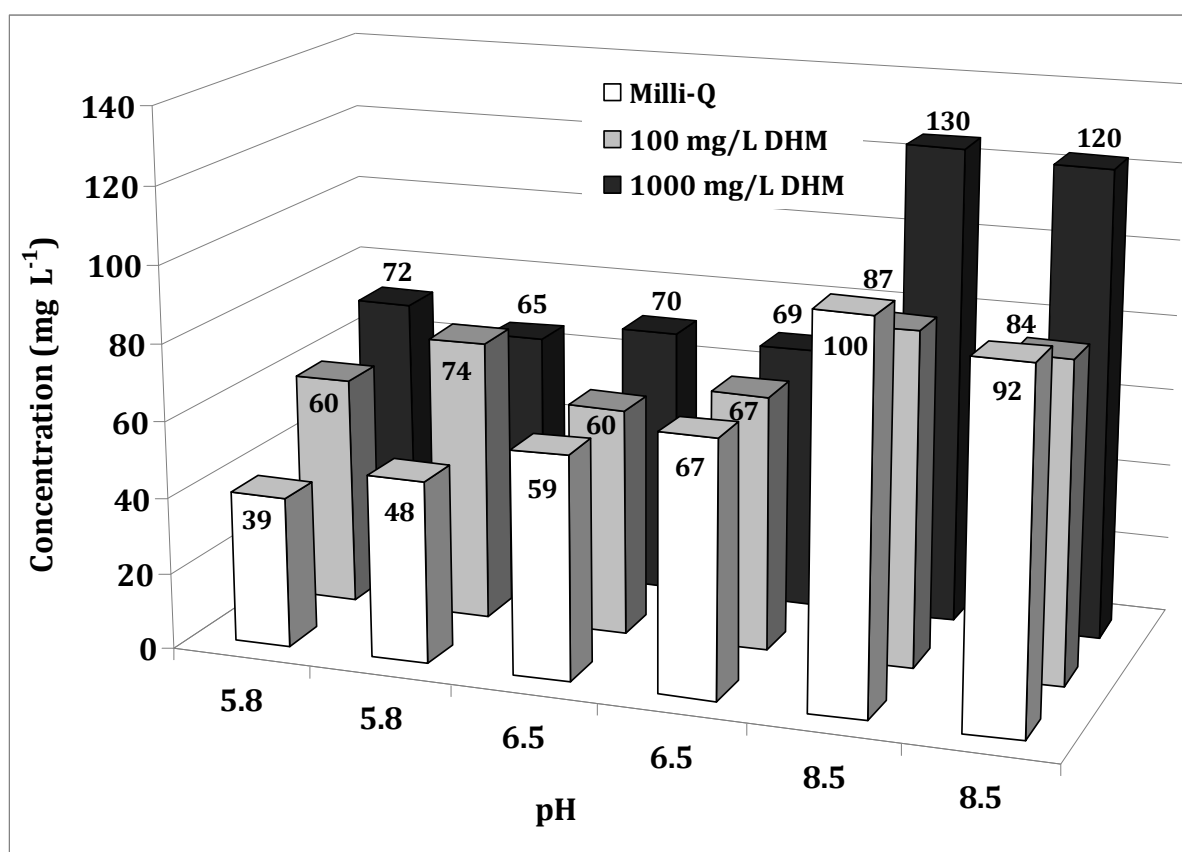


439
440 **Figure 4: TCIPP concentrations (mg L⁻¹) in leachate produced during 24 h single batch**
441 **experiments (run in duplicate) examining TCIPP leaching from PUF at different**
442 **temperatures and DHM concentrations in leaching fluid. Data labels on bars are rounded**
443 **to two significant figures.**

444

445

446



447

448 **Figure 5: TCIPP concentrations (mg L⁻¹) in leachate produced during single batch**
449 **experiments examining TCIPP leaching from PUF at different pH values and DHM**
450 **concentrations in leaching fluids. Data labels on bars are rounded to two significant**
451 **figures.**

452

Highlights

- We study TCIPP leaching from furniture polyurethane foam (PUF)
- Leaching of TCIPP from PUF appears to be a first order process
- In serial batch leaching tests, >95 % of TCIPP was depleted from PUF after 168 h
- TCIPP concentrations between 13 mg L^{-1} – 130 mg L^{-1} were detected in the leachate
- leaching is potentially a significant pathway of environmental TCIPP emissions